

# Chemical composition and surface property of kaolins

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## Abstract

The crystal structure, crystal chemistry and surface properties of kaolinite in kaolin clays have been studied. The crystallinity index was lower for hard kaolin than for soft kaolin. The floatability of hard kaolin was lower than that of soft kaolin. Hard kaolin was the dominant kaolin in bauxite. A new type of collector for hard kaolin was studied in order to selectively separate kaolin from diasporite in bauxite. The surface zeta potential variation of the hard kaolin as a function of pH was almost the same as that of the soft kaolin. The IEP of the hard kaolin varied from 2.5 to 3.8. The SiO<sub>2</sub> (wt%) content of the several kaolins showed negative correlations with IEP, but Al<sub>2</sub>O<sub>3</sub> (wt%) content showed positive correlation with IEP. The crystallinity index of kaolinite was not the major factor determining IEP. In the broad range of pH, the negative potential of the hard kaolin was lower than that of the soft kaolin. At the point (pH = 7.3±) of zero net proton charge at the edge of the kaolinite, TFe (wt%) showed negative correlation with surface zeta potential of the kaolin, but the crystallinity index of kaolinite showed a positive correlation.

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## 1. Introduction

Each kaolinite layer comprises one octahedral sheet and one tetrahedral sheet. Kaolinite layers are less tightly bound together in the *c* direction, by hydrogen bonding between hydroxyl sites on the gibbsite basal plane and the oxygens of the silicon tetrahedral sheet. Kaolinite has different surface structures between base planes and edge planes. (001) plane is its base plane. (110) and (010) planes are the edge planes. Thus, kaolinite is known to have a heterogeneous surface charge. The surface electric properties of kaolinites have been investigated by many authors (Hussain et al., 1996; Wieland and Stumm, 1992; Herring et al., 1992; Newman, 1987; Rand and Melton, 1977; Schofield and Samson, 1954; Williams and Williams, 1978; Brady et al., 1996; Yuan and Pruett, 1998; Tari et al., 1999; Johnson et al., 2000). The basal surfaces of kaolinite are believed to carry a constant structural charge due to the isomorphous substitution of Si<sup>4+</sup> by Al<sup>3+</sup>, whereas the charge on the edges is due to the protonation/deprotonation of exposed hydroxyl groups and depend on the

solution pH, though later studies (Johnson et al., 2000) suggested that the charge on the basal surface has a possible pH dependence.

It has been shown that an edge surface which should carry a positive double layer in acid solution, and a negative double layer in alkaline solution, with a point of zero charge (PZC) in the neighborhood of pH 7, dependent on the particular kaolinite crystal structure (Newman, 1987). Rand and Melton showed that curves of Bingham yield stress of homoionic Na kaolinite suspensions as a function of pH all intersect at one point, the iso-electric point of the edge surface of the kaolinite (Rand and Melton, 1977). This point was pH 7.3 ± 0.2. This value agreed closely with that of Schofield and Samson (1954) from adsorption of chloride ions, and with the point of zero charge as deduced from the hydrogen and hydroxyl adsorption measurements of Flegmann et al. (Herring et al., 1992), although it did not agree with their recommended value of 5.8. The experimental values of the point of zero net proton charge (PZNPC) of the edge surface ranged from 7 to 8 (Rand and Melton, 1977). Williams and Williams (1978) calculated a value of PZNPC = 7.3 for the edge surface of kaolinite by linearly combining the potentials of quartz and aluminum oxide. Because of high face area to edge area ratio, the kaolinite particles carry an overall net negative charge, though they can carry a low net

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positive charge in low solution pH (Williams and Williams, 1978; Brady et al., 1996). Clays from five different commercial deposits in Georgia were studied to understand the variations of zeta potential and related fundamental properties (Yuan and Pruett, 1998). The results suggest that higher negative zeta potential is related to exchangeable or soluble calcium ions in the clays. The charge properties of well and poorly ordered kaolinite and halloysite-7 Å were studied (Tari et al., 1999). The curves of zeta potential vs. pH showed the same pH dependency for the three minerals, but a gradual increase of zeta potential when passing from well ordered kaolinite to halloysite-7 Å through the poorly ordered kaolinite.

Zeta potential represents the electric potential at the shear plane between a particle and the surrounding liquid when the charged particle moves in an electric field (Brady et al., 1996; Wang and Hu, 1988). It is one of the most important surface properties of minerals determining the effectiveness of commercial mineral separation processes such as flotation. Although the floatability of the kaolinite was researched (Köster et al., 1992; Choi et al., 1993), the gap in the flotation behavior between hard kaolin and soft kaolin has seldom been studied. In bauxite flotation research, it was found that the flotation behavior between hard kaolin and soft kaolin was different. To understand the mechanism of kaolin flotation, it is imperative to understand how zeta potential varies in the kaolins. This paper investigates the effect of the crystal structure, chemical composition and other mineralogical properties of kaolins and kaolinites on their surface charge properties and the surface iso-electric points (IEP).

## 2. Experimental

### 2.1. Materials

Kaolin clays from four different deposits were collected for this study. Sample Ka-ML from Hunan Miluo was representative of the so-called “soft kaolin” type. The other three samples Ka-JX, Ka-DYG, Ka-MC were from Henan Jiaxian, Henan Dayugou and Henan Mi-anchi respectively. They were of the “hard kaolin” type. The chemicals used in the present study include: acetic acid (AR), dodecyl amine (AR) and hexadecyl trimethyl ammonium bromide (AR). HCl and NaOH (AR) were used for pH adjustment. The high-purity water used in the experiments was distilled water.

### 2.2. Methods

A powder diffractometer (Shimadzu) was run in the reflection mode with graphite-filtered Cu-K $\alpha$  radiation (50 mV, 100 mA), and a goniometer speed of 4° 2 $\theta$ /min.

The powder diffraction patterns with a 0.01° precision of d-spacing measurements were conducted from 5° to 85° (2 $\theta$ ).

The zeta potential was measured by standard procedures on a Brookhaven Zeta Plus Zeta potentialmeter. The kaolin was added into a 100 ml beaker. The solid concentration was about 0.02%. The suspension was agitated for 2 min and transferred to the testing vessel, after which the zeta potential measurement was made. pH was measured to an accuracy of  $\pm 0.02$  (REX Model PHS-3C pH meter) and unless otherwise stated the pH is that of the stationary suspension. For each condition, at least three suspensions were prepared and measured. The measurement error was found to be within 5 mV.

Flotation tests were conducted in a 40 ml micro flotation cell on a XFG type flotation-machine. For each test, 3 g of mineral samples were added to 35 ml of water, agitated with a magnetic stirrer. After sequential addition of pH modifiers and collectors, the suspension was conditioned for 1 and 3 min, respectively. Flotation time was fixed at 4 min.

## 3. Results and discussion

### 3.1. XRD

Kaolinite crystal structure is highly complex, due to the large number of stacking faults that may appear during its formation and growth. The XRD methods usually employed to study kaolinite order only provide an approximation of the real structure. There are many factors influencing kaolinite order such as stacking layer disorder, cation distribution disorder, non-plane layer structure, machine disorder etc. The Hinckley index (usually abbreviated as HI) is one of the most widely used crystallinity indices to express kaolinite order (Zhang, 1987; Ma, 2000). Kaolinite is considered to be well ordered if its Hinckley index (HI) > 0.9 (Aparicio and Galan, 1999). The XRD patterns from the four samples examined are shown in Fig. 1. According to the scale proposed by Hinckley, the crystallinity index (HI) of kaolinite in kaolin clays were calculated (Table 1). The HI value of kaolinite in soft kaolin Ka-ML was larger than that in hard kaolins Ka-JX, Ka-DYG and Ka-MC. Kaolinite in soft kaolin Ka-ML corresponds to well ordered kaolinite, whereas those in the three hard kaolins correspond to poorly ordered kaolinite.

X-ray diffraction analysis indicated that all four clays were essentially comprised of kaolinite. Illite is a minor component in Ka-DYG and Ka-MC samples, which contained no more than 10 wt% of this mineral, it not being found in any other mineral except kaolinite in Ka-ML and Ka-JX samples. Hard kaolin is the dominant kaolin in bauxite as the Ka-MC sample was collected in bauxite horizon.

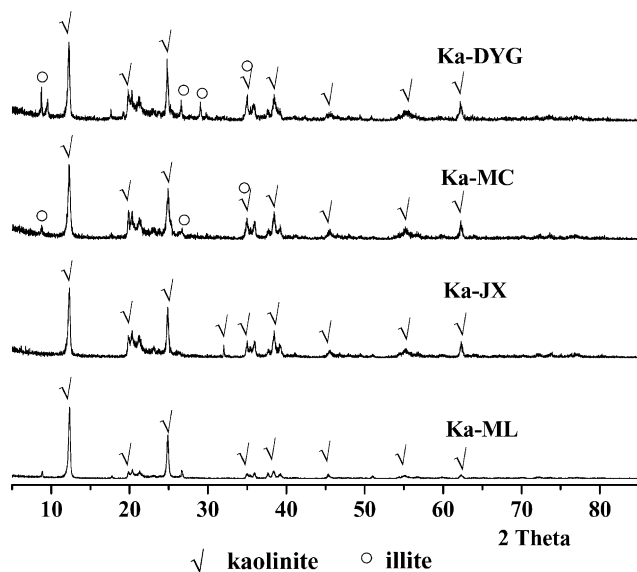


Fig. 1. Power X-ray diffraction plots of the different kaolin clays.

### 3.2. Zeta potentials of the kaolin clays as a function of pH

The zeta potentials of the kaolin clays are shown in Fig. 2 as a function of pH. Table 2 lists the iso-electric point (IEP) of the kaolin clays. The surface zeta potential variation of the hard kaolins as a function of pH is almost the same as that of the soft kaolin. The iso-electric point (IEP) of the different kaolins is almost the same, but there were significantly different zeta potentials among the four kaolin samples when measured under the same conditions. In the broad range of pH, the zeta potential of the hard kaolin was lower than that of the soft kaolins. The iso-electric point (IEP) of the hard kaolins varies from 2.5 to 3.8. The reason was that the zeta potential is dependent on the solution pH, ionic strength of the suspension and surface properties of kaolinite particles. The ionic strength of the suspension was closely dependent on the contents of all mineral phases, the crystal imperfections, chemical compositions, crystal forms and crystal surface structure.

### 3.3. Chemical compositions

The chemical analysis results are shown in Table 3. On the basis of phase analysis, titanium in the samples generally comes from anatase; iron could be present in iron-containing minerals (such as goethite) or colloidal particles, as well as in the kaolinite crystal structure.

Table 1  
Crystallinity index of kaolinite in two kinds of kaolin clays

| No.    | Location      | Sample      | Crystallinity index (HI) | Note                    |
|--------|---------------|-------------|--------------------------|-------------------------|
| Ka-ML  | Hunan Miluo   | Soft kaolin | 1.00                     | Weather-eluviation type |
| Ka-JX  | Henan Jiaxian | Hard kaolin | 0.77                     | In coal-bearing strata  |
| Ka-MC  | Henan Mianchi | Hard kaolin | 0.82                     | In bauxite horizon      |
| Ka-DYG | Henan Dayugou | Hard kaolin | 0.74                     | In coal-bearing strata  |

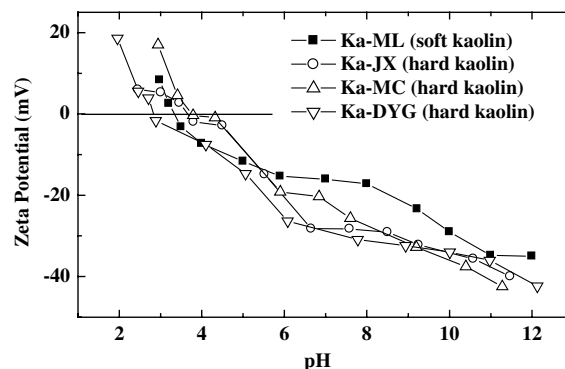


Fig. 2. Zeta potentials of the different kaolins as a function of pH.

Table 2  
The iso-electric point (IEP) of the different kaolins

| Ka-ML | Ka-JX | Ka-MC | Ka-DYG |
|-------|-------|-------|--------|
| 3.34  | 3.62  | 3.78  | 2.82   |

Potassium and sodium were closely related to illite and muscovite.

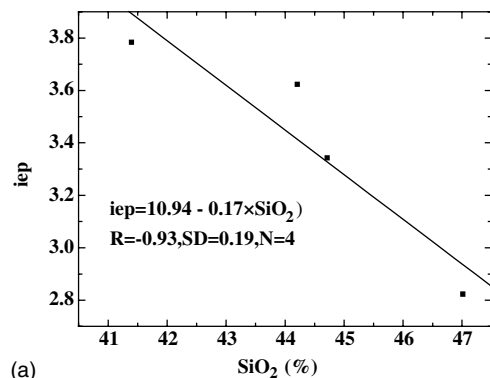
Two selected plots of the oxide percentages vs. the iso-electric point (IEP) for the four samples are shown in Fig. 3.  $\text{SiO}_2$  (wt%) of the kaolin clays shows negative correlation with IEP. Its correlation coefficient was  $-0.93$ ; but  $\text{Al}_2\text{O}_3$  (wt%) shows positive correlation with IEP. Its correlation coefficient was  $0.77$ . The other chemical compositions such as the contents of  $\text{K}_2\text{O}$ ,  $\text{Na}_2\text{O}$ ,  $\text{MgO}$  and  $\text{TiO}_2$  in Table 3 show little correlation with IEP. Because the iso-electric point of the edge surface of the kaolinite was  $\text{pH } 7.3 \pm$ , the surface zeta potential of the kaolinite may mainly represent the electric potential at the shear plane between the surrounding liquid and the base plan (001) surface.

Fig. 4 plots the zeta potential ( $\text{pH } 7.3 \pm$ ) vs. chemical composition (oxides wt%) of the different kaolins. At the point of solution  $\text{pH } 7.3 \pm$ , the surface zeta potential shows negative correlation with TFe (wt%) of the kaolin clays. Its correlation coefficient was  $-0.99$ ; whereas, the surface zeta potential shows positive correlation with  $\text{Al}_2\text{O}_3$  (wt%) of the kaolin clays; its correlation coefficient was  $0.76$ . The results from this study suggest that ferrous ions were readily released into the solution as electrolytes. Higher negative zeta potential is related to a higher level of exchangeable or soluble ferrous ions in clays.

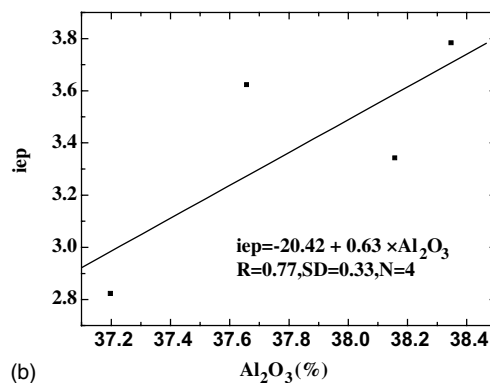
Table 3

The compositions of the kaolin samples (wt%)

| No.    | Sample      | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | MgO   | CaO   | TFe  | TiO <sub>2</sub> | K <sub>2</sub> O | Na <sub>2</sub> O |
|--------|-------------|------------------|--------------------------------|-------|-------|------|------------------|------------------|-------------------|
| Ka-ML  | Soft kaolin | 44.73            | 38.16                          | 0.023 | 0.059 | 0.11 | 0.05             | 0.15             | 0.056             |
| Ka-JX  | Hard kaolin | 44.22            | 37.66                          | 0.093 | 0.074 | 0.54 | 0.22             | 0.064            | 0.049             |
| Ka-MC  | Hard kaolin | 41.41            | 38.35                          | 0.33  | 0.098 | 0.39 | 1.68             | 0.83             | 0.094             |
| Ka-DYG | Hard kaolin | 47.03            | 37.20                          | 0.071 | 0.110 | 0.67 | 0.69             | 1.03             | 0.2               |



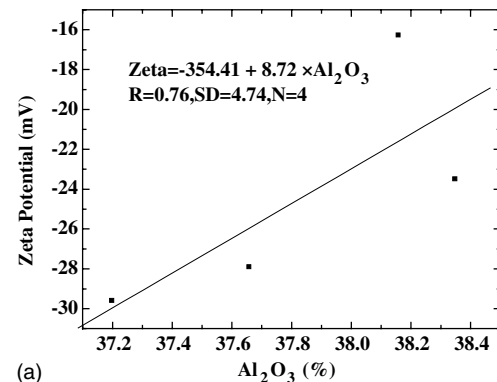
(a)



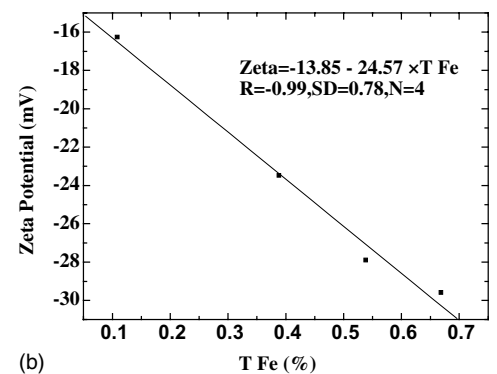
(b)

Fig. 3. Plots of the iso-electric point (IEP) vs. chemical composition (oxides wt%) of the different kaolins: (a) the oxides wt% of SiO<sub>2</sub> and (b) the oxides wt% of Al<sub>2</sub>O<sub>3</sub>.

Fig. 5 shows that there is some relationship between the crystallinity index (HI) of kaolinites and the iso-electric point (IEP) of the different kaolins. Its correlation coefficient was 0.17. The result suggests that the crystallinity index (HI) of kaolinites is not the major factor determining the iso-electric point (IEP) of the kaolins. Fig. 6 suggests that the surface zeta potential shows negative correlation with the crystallinity index (HI) of kaolinites at the point of solution pH 7.3±. Its correlation coefficient was 0.99. Because the iso-electric point of the edge surface of the kaolinite was pH 7.3±, the surface zeta potential of the kaolinite may mainly represent the electric potential at the shear plane between the surrounding liquid and the base plan (001) surface. The result suggests that at the point of solution pH 7.3±, the larger the crystallinity index (HI) of kaolinites is, the higher is the electric potential at the shear



(a)



(b)

Fig. 4. Plots of the zeta potential (pH = 7.3) vs. chemical composition (oxides wt%) of the different kaolins: (a) the oxides wt% of Al<sub>2</sub>O<sub>3</sub> and (b) the oxides wt% of TFe.

plane between the surrounding liquid and the base plan (001) surface was.

### 3.4. Flotation experiments

The studies of the influence of the different agents on Ka-JX hard kaolin and Ka-ML soft kaolin were followed up by laboratory flotation tests. With dodecyl amine acetate ( $2 \times 10^{-4}$  M) or cetyl trimethyl ammonium bromide ( $2 \times 10^{-4}$  M) as collector, the recovery of Ka-JX hard kaolin was lower than that of Ka-ML soft kaolin at different solution pH (shown in Figs. 7 and 8). Fig. 9 shows the effect of dodecyl amine acetate concentration on the flotation recovery of different kaolins. The measurements were carried out at the solution pH 2.4. The more dodecyl amine acetate added, the higher the recovery of different kaolins was achieved. When the

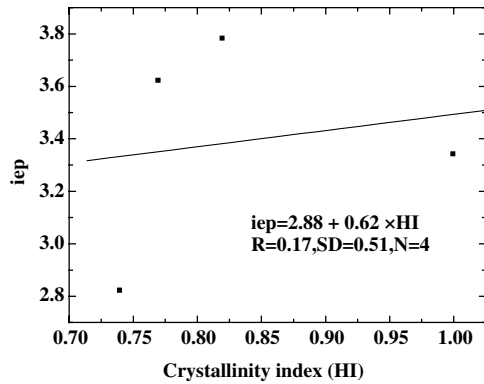


Fig. 5. Plots of the crystallinity index (HI) of kaolinites vs. the surface iso-electric points (IEP) of the different kaolins.

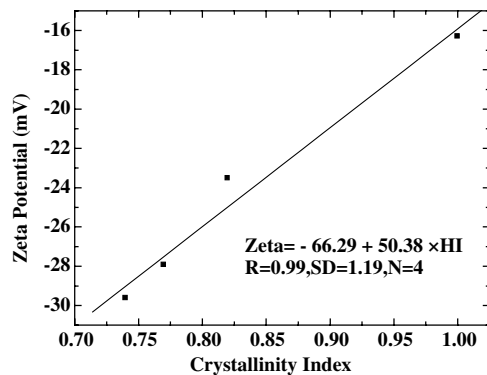


Fig. 6. Plots of the crystallinity index (HI) of kaolinites vs. the zeta potential ( $pH = 7.3 \pm$ ) of the different kaolin.

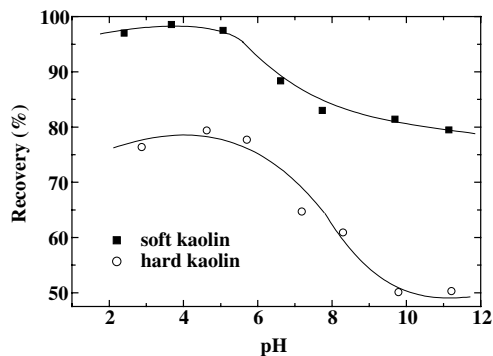


Fig. 7. Flotation recovery of the different kaolin vs. pH with a collector of dodecyl amine acetate ( $2 \times 10^{-4}$  M).

amount of dodecyl amine acetate added was more than  $2 \times 10^{-4}$  M, the recovery of Ka-ML soft kaolin approached 100%, whereas that of Ka-JX hard kaolin was 80%.

There were apparent differences between soft kaolin and hard kaolin in the crystal structure, crystal chemistry and surface property of kaolinite in kaolin clays, as well as in structure of clays. The crystallinity index is

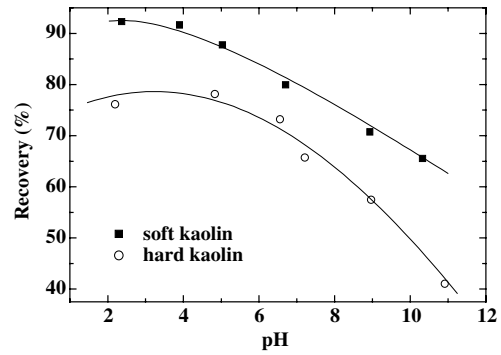


Fig. 8. Flotation recovery of the different kaolin vs. pH with a collector of cetyl trimethyl ammonium bromide ( $2 \times 10^{-4}$  M).

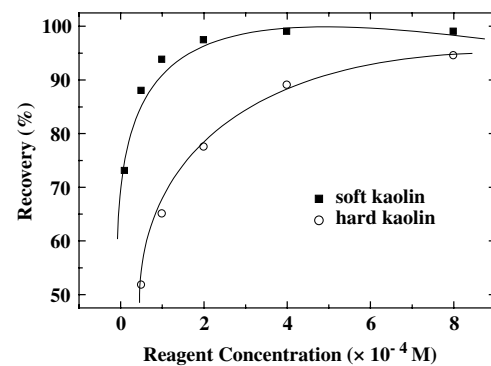


Fig. 9. Effect of dodecyl amine acetate concentration on the flotation recovery of different kaolins at pH 2.4.

lower for hard kaolin than for soft kaolin, such that the floatability of hard kaolin was lower than that of soft kaolin. Weaver and Pollard (1983) submitted that poorly ordered hard kaolins associated face surfaces of kaolinite to face surfaces of kaolinite (“FF”) flocculation in sea-water, whereas well ordered soft kaolins maybe associated edge surfaces of kaolinite to face surfaces (“EF”) flocculation in freshwater. The soft kaolin had more pore space than the hard kaolin. The rock hardness of the hard kaolin was high. The major textures of the hard kaolin clay were detrital texture, cryptocrystalline texture and fluxion texture etc. The essential mineral kaolinite approximately directionally arrayed in the hard kaolin clay. After the hard kaolin clay had been ground, the particles, which consisted of “FF” kaolinites, would flocculate in the solution. The particles of hard kaolin would disperse at the approximate point ( $pH = 7.3 \pm$ ) of zero net proton charge of edge surface of the kaolinites. The well ordered soft kaolin loosely aggregated. The essential mineral kaolinite may form the soft kaolin clay in edge surfaces to face surfaces (“EF”) of kaolinite. The soft kaolin particles were prone to dispersal in the solution and to reaction with the agents. Therefore, the floatability of soft kaolin is higher than that of hard kaolin.

#### 4. Conclusion

The surface zeta potential variation of the hard kaolins as a function of pH was almost the same as that of the soft kaolin. The IEP of the hard kaolins varied from 2.5 to 3.8. SiO<sub>2</sub> (wt%) of the several kaolins showed negative correlation with IEP, but Al<sub>2</sub>O<sub>3</sub> (wt%) showed positive correlation with IEP. The crystallinity index of kaolinites was not the major factor determining IEP. In the broad range of pH, the negative potential of the hard kaolin was lower than that of the soft kaolin. At the point (pH = 7.3±) of zero net proton charge of edge of the kaolinite, TFe (wt%) showed negative correlation with surface zeta potential of the kaolin, but the crystallinity index of kaolinite showed positive correlation. The mineral–solution interface reaction played a pivotal role in determining the surface zeta potentials of the kaolins. More work is needed to fully understand the surface properties and floatabilities of kaolins.

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